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Chemiluminescent properties of polymeric blue fluorophores containing diphenylanthracene unit

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Abstract

New conjugated and non-conjugated alternating block copolymers containing 9,10-diphenyl-2-chloroanthracene moieties in the main chain were synthesized via Williamson synthesis for the blue chemiluminescent fluorophore. UV-vis absorption and luminescent characteristics including chemiluminescence were measured and compared with model fluorophore 9,10-bis(*p*-methoxyphenyl)-2-chloroanthracene. Polymers displayed blue photoluminescence in solution with maximum around 430 nm. Tetramethyl ammonium salicylate-catalyzed reaction of hydrogen peroxide with bis(2-carbopentyloxy-3,5,6-trichlorophenyl)oxalate produced a strong chemiluminescent blue light emission with wavelength of 440 nm in the presence of the polymeric fluorophore. The chemiluminescent intensity decayed exponentially and the glow of chemiluminescence maintained more than 12 h and was visible with naked eye.

Keywords: 9; 10-Diphenyl-2-chloroanthracene; Polyether; Polymeric blue fluorophore; Chemiluminescence

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1. Introduction

Conventional chemiluminescent fluorophores were highly conjugated aromatic compounds such as *N*,*N*′-bis(2,6-diisopropylphenyl)-1,6,7,12-tetrakis (*p*-*tert*-butylphenoxy)-3,4,910-perylene tetracarboxydiimide, rubrene, 9,10-bis(*p*-methoxyphenyl)-2-chloroanthracene and 9,10-bis(phenylethynyl)-2-chloroanthracene derivatives [1–3].

A few examples appeared in the literature applying the polymeric fluorophores to chemiluminescent reaction. They are generally more tractable and stable than molecular fluorophores. Tuned light can be accomplished by copolymerization of the controlled amount of chromophore monomers. Moreover the solubility properties can be variable according to the chemical structure of spacer monomers. Various polydistyrylarylenes containing 1,4-bis(2′,2′-diphenylvinyl)benzene, 1,4-bis(2′-phenylvinyl)benzene [4,5], fluorene and carbazole units [6] were adopted as blue light-emitting chemiluminescent fluorophores. But the serious degradation was observed for the polydistyrylarylene chromophore during chemiluminescent reaction. The initial chemiluminescent light changes gradually in the CIE coordination because of their labile oxidation of phenylenevinylene linkage. Among the chemiluminescent fluorophores, especially blue

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fluorophores having anthracene moiety have been widely used in commercial and industrial application because of stability in peroxide oxidative conditions. More recently, it was reported that perylene tetracarboxydiimide- and diphenylanthracene-containing polyester was used as an efficient violet color (625 nm) light-emitting fluorophores during chemiluminescent reaction [7,8]. The blue shift was observed for the polyester and polyurethane chromophores because the blue chromophore was linked with electron donating oxycarbonyl or urethane linkage.

In this report, 9,10-diphenyl-2-chloroanthracene-containing new polyether blue fluorophores linked with electron donating alkoxy moiety were prepared and their chemiluminescent characteristics were examined.

2. Experimental

2.1. Chemicals and instruments

9,10-Bis (*p*-methoxyphenyl)-2-chloroanthracene (**1**), 9,10-bis (*p*-hydroxyphenyl)-2-chloroanthracene (**2**) [8] and bis(2-carbopentyloxy-3,5,6-trichlorophenyl)oxalate (CPPO) [9] were prepared by the method previously reported. 1,2-Dichloroethane and 1,6-dichlorohexane were purified by distillation. *N,N*-Dimethylacetamide (DMAc) was purified by vacuum distillation after drying by azeotropic distillation with benzene using Dean–Stark separator. Potassium carbonate (Aldrich Chem. Co., 99.99%), tetramethyl ammonium salicylate (Aldrich Chem. Co.), *t*-butanol, dibutylphthalate (GR, Yakuri Co.) and dimethylphthalate (GR, Junsei Chem.Co.) were used without further purification.

FT-IR spectra were obtained with a Midac Model M-1200 spectrophotometer and ^{1}H NMR spectra were recorded on a Varian Gemini-2000 spectrometer. UV spectra were obtained on a Shimadzu model UV-2100S spectrophotometer. Gel permeation chromatography (GPC) data were obtained with a Waters HPLC using three columns (μ-Styragel 10^2, 10^3 and 10^4 Å) in THF and calibrated with polystyrene standards at 20 °C. Intensity of the emission light was measured with a Minolta Chromameter CS-100. Photoluminescence were measured on an Optical Spectra Multichannel Analyzer (OSMA-1000, Photodiodes 1024).

2.2. Representative preparation of polyether containing diphenylanthrcene units

In a round-bottomed flask (250 ml) equipped with a Dean-Stark separator, were placed 9,10-bis(*p*-hydroxyphenyl)-2-chloroanthracene (2, 39.65 g, 0.10 mmol), 1,6-dichlorohexane (15.51 g, 0.10 mmol), potassium carbonate (16.58 g, 0.12 mol), dry DMAc (150 ml) and toluene (80 ml). The solution was maintained at 120 °C for 18 h and was refluxed at 150 °C for 6 h to eliminate water. After the reaction was completed, propyl bromide (5 g) was added and the reaction mixture was further reacted for 12 h. The final reaction mixture was poured into ice water to precipitate the reaction product. The solid product was filtered and washed with water/ethanol (1/2). The powdery polymer was dissolved in tetrahydrofuran and reprecipitated into diethyl ether to yield **4**. The other polymer (**3**) was synthesized by similar procedures.

3: Yield 72%. FT-IR (KBr) 3125–3010 (aromatic *C–H*), 2994–2860 (aliphatic *C–H*), 1615–1532 (aromatic *C=C*), 1240–1035 (*C–O*) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 6.9–7.6 (m, 15 H, 2-*O-Ph-* and anthracene ring), 3.8 (s, 4 H, 2-CH_2-). Anal. calcd for $C_{28}H_{19}ClO_2$ (Mw, 422.91): C, 79.52; H, 4.53. Found:C, 79.32; H, 4.48.

4: Yield 60%. FT-IR (KBr) 3125–3010 (aromatic C–H), 2990–2870 (aliphatic *C–H*), 1615–1530 (*C=C*), 1240–1025 (*C–O*). ^{1}H NMR ($CDCl_3$) δ 6.8–7.6 (m; 15 H, 2 *–O–Ph–* and anthracene ring), 3.8 (t; 4 H, 2–OCH_2–), 1.8–1.4 (m, 8H, –$CH_2CH_2CH_2CH_2$–). Anal. calcd for $C_{32}H_{27}ClO_2$ (Mw, 478.51): C, 80.25; H, 5.68. Found: C, 80.36; H, 5.56.

2.3. Examination of the chemiluminescent property

Polymeric fluorophore (**3**) (3×10^{-5} M) and bis (2 - carbopentyloxy - 3,5,6 - trichlorophenyl)oxalate (CPPO, 1.95×10^{-3} M) were dissolved in dibutylphthalate (20 ml) at 80 °C under nitrogen. On the other hand, hydrogen peroxide (90%, 1.5 equivalent of CPPO) and tetramethyl ammonium salicylate (2.5×10^{-5} M) were dissolved in 20 ml of mixed solvent of dimethylphthalate/*t*-butanol (5/1).

Chemiluminescence devices can be easily prepared by putting a solution of catalyst and hydrogen peroxide (1.0 ml) into the polypropylene tube (ID, 4 mm; l, 60 mm). A sealed glass capillary tube containing a solution of fluorophore and CPPO (3.0 ml) is placed in the polypropylene tube and then the tube is sealed. Rates of catalytic decomposition of CPPO were determined by monitoring the decay intensity of chemiluminescent fluorophore solutions. The sample was bent to break and placed in the thermostatic sample block of the chemiluminescence-measuring luminometer.

3. Results and discussion

3.1. Preparation and characterization of polymeric fluorophores

Blue chromophore monomer, 9,10-bis(*p*-hydroxyphenyl)-2-chloroanthracene (**2**) was prepared by the method previously reported [8]. Model blue fluorophore 9,10-bis(*p*-methoxyphenyl)-2-chloroanthracene (**1**) represents the reference structure for comparison with the new polymers. The Williamson-type polycondensation, used to synthesize polymers, was easily accomplished by the reaction of α,ω-dichloroalkane and **2** in the presence of potassium carbonate as illustrated in Scheme 1.

Table 1 summarizes the results of the preparation of polymeric fluorophores.

The fluorophores were characterized through the data from proton NMR, IR and elemental analyses. In the FT-IR spectra of the polymer samples, bands were found in the 1250–1020 cm^{-1} regions attributable to C–O stretching of the fluorophores **3** and **4**. In the aliphatic regions of the ^1H NMR spectra, all samples showed a singlet peak at 3.80 ppm assignable to $–OCH_2–$. The doublet at 6.8 ppm was corresponding to aromatic protons at 2,6-position of –O–Ph–. On the other hand, the multiplet peak at 7.2 ppm is attributed to the proton of 3,5-position of –O–Ph– and the anthracene ring protons. The CHN elemental analysis values matched well with the data calculated from the expected chemical structure.

Data from the GPC analysis are shown in Table 1. The weight average molecular weights (Mw) of polymers **3** and **4** were 12,600 and 15,800 with a molecular weight distribution (MWD) of 2.34 and 2.02, respectively. Polymers **3** and **4** showed a moderately high molecular weight. Polymers were soluble in common organic solvents such as chloroform, tetrahydrofuran and dibutylphthalate. The solubility data are summarized in Table 2.

Table 1
Results of preparation of model and polymeric fluorophores

Fluorophores	Mn[a]	Mw/Mn (MWD)[b]	Yield (%)
1	424.5	–	68[c]
3	12,600	2.34	72
4	15,800	2.02	60

[a] Mn, number-average molecular weight.

[b] Mw, weight-average molecular weight; MWD, molecular weight distribution.

[c] Yield was obtained from *p*-methoxyphnylmagnesium bromide and 2-chloroanthraquinone.

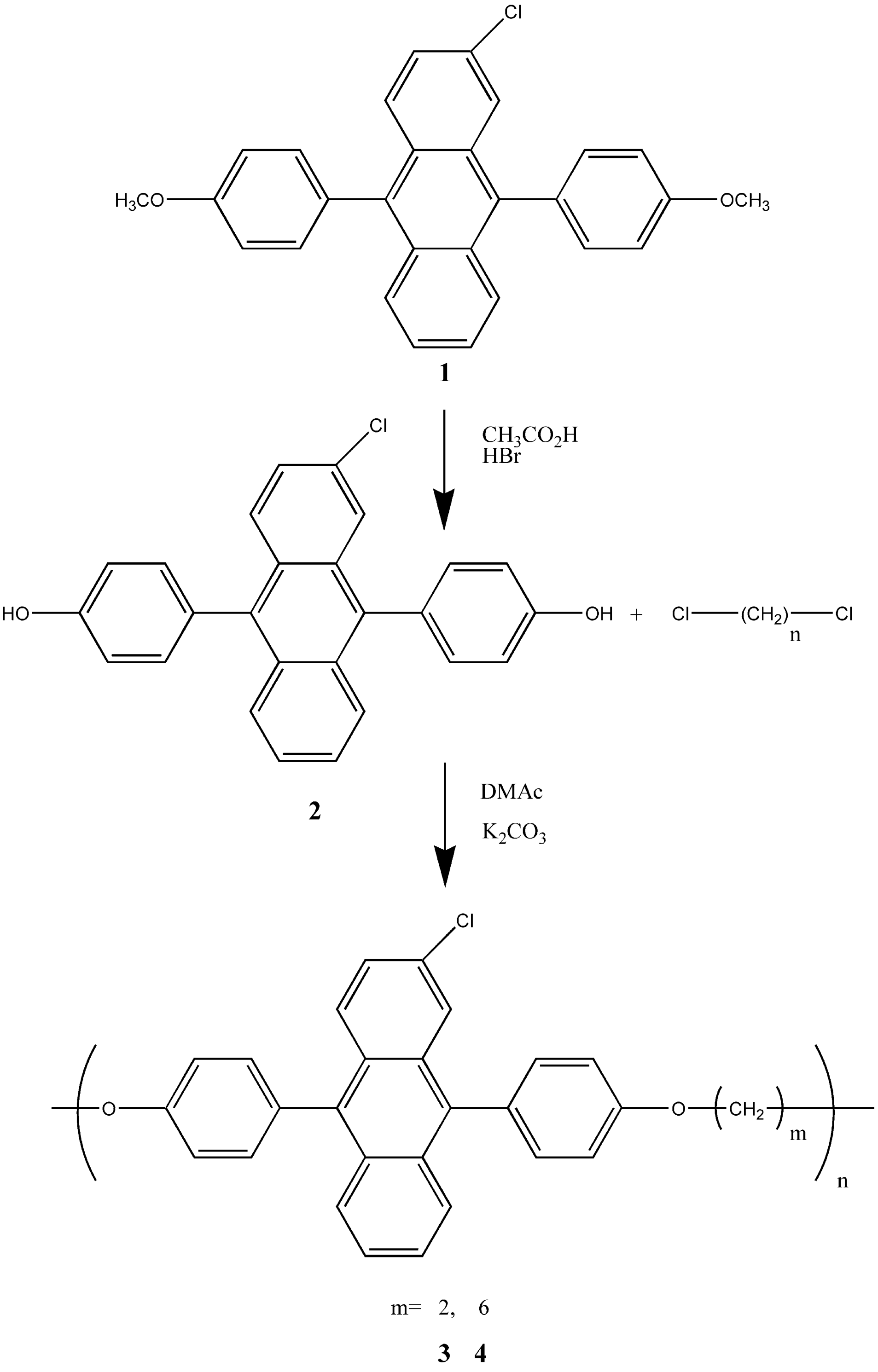
3.2. Optical properties

The UV absorbance, photoluminescence as well as the chemiluminescent characteristics of model and polymeric fluorophores were measured and listed in Table 3. UV absorbance of a series of polymers **3** and **4** in dilute solution were measured and compared with that of the corresponding model compound **1**. The characteristic maximum

Table 2
Solubility of model and polymeric fluorophores

Fluorophores	NMP	DMAc	THF	$CHCl_3$	DBP	EtOH	Benzene	Toluene	Hexane
1	+	+ +	+ +	+ +	+ +	+	+	+	–
3	+	+	+ +	+ +	+ +	+	+	+	–
4	+	+	+ +	+ +	+ +	-	+	+	+

NMP, *N*-methylpyrrolidinone; DMAc, *N,N*-dimethylacetamide; THF, tetrahydrofuran; DBP, dibutyl phthalate.


Cl
H3CO
OCH3
1
CH3CO2H
HBr
Cl
HO
OH
+
Cl
(CH2)
n
Cl
2
DMAc
K2CO3
Cl
O
O
CH2
m
n
m= 2, 6
3 4

Scheme 1.

Table 3
The UV-vis absorption, photoluminescent and chemiluminescent maximum wavelength of the model and polymeric fluorophores

Fluorophores	UV(λ_{max})[a]	PL(λ_{max})[a]	CL(λ_{max})[b]	CIE Color coordinate[c]	
				After 1 min	After 4 h
1	362.0, 381.5, 402.5	432.5	445.1	$x=0.1438$ $y=0.0752$	$x=0.1651$ $y=0.1563$
3	362.1, 381.3, 403.0	431.2	442.0	$x=0.1442$ $y=0.0978$	$x=0.1831$ $y=0.1712$
4	362.1, 381.2, 402.6	430.3	441.3	$x=0.1593$ $y=1.1512$	$x=0.2092$ $y=0.1959$

[a] Measured in chloroform solution.
[b] Measured in dibutylphthalate solution.
[c] Measured during chemiluminescent reaction.

absorption of **1**, **3** and **4** were exhibited at the same wavelength region as shown in Fig. 1. The UV-vis absorption of **1**, **3** and **4** remain nearly uninfluenced by the substituents: **1** corresponds to model fluorophore with simple methoxy substituent and **3** to ethyleneoxy-substituted polymeric fluorophore. The same results are obtained for **4**. All of them exhibited the first absorption band around 260 nm assigned to the aromatic groups and the next four absorptions at 325–425 nm, which is characteristic of the 9,10-diphenylanthracene structure [10,11].

Polyethers **3** and **4** were compared with the corresponding polyester containing a 9,10-diphenylanthracene unit, which was previously prepared in our laboratory. The electron donating alkyleneoxy groups in the polyethers **3** and **4** enrich the electron density of the anthracene ring. The blue shift was observed for the polymer having the electron withdrawing oxycarbonyl group as shown in Fig. 1d). This supported the fact that the alkoxy substituent reduced the electronic band gap and caused by a red shift by 3 nm. The results of the investigation of photoluminescence for model

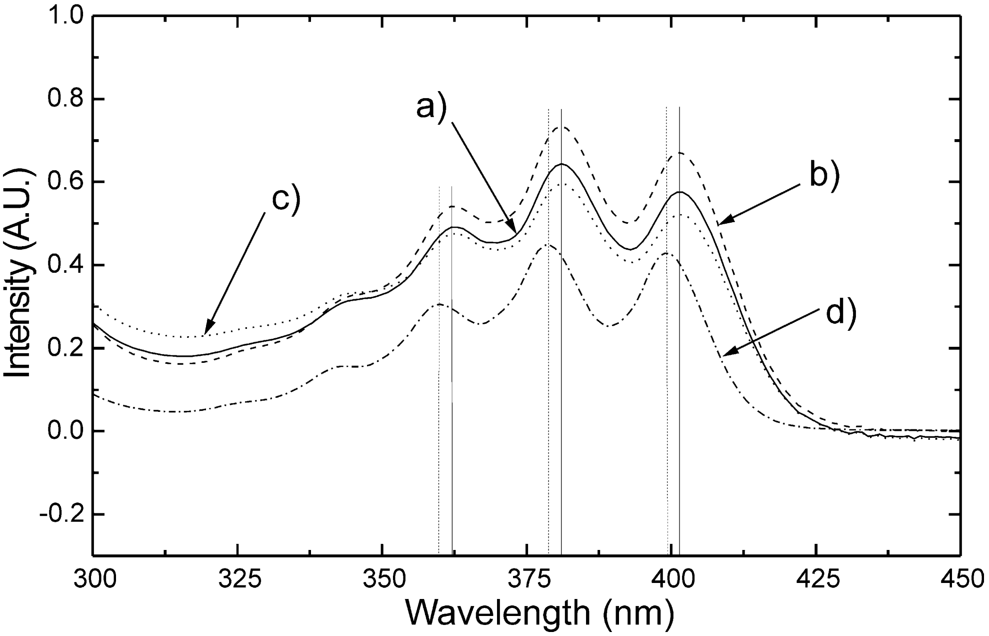


Fig. 1. UV-vis absorption spectra of (a) **1**, (b) **3**, (c) **4** and (d) polymers obtained from 9,10-bis(p-hydroxyphenyl)-2-chloroanthracene and sebacoyl chloride.

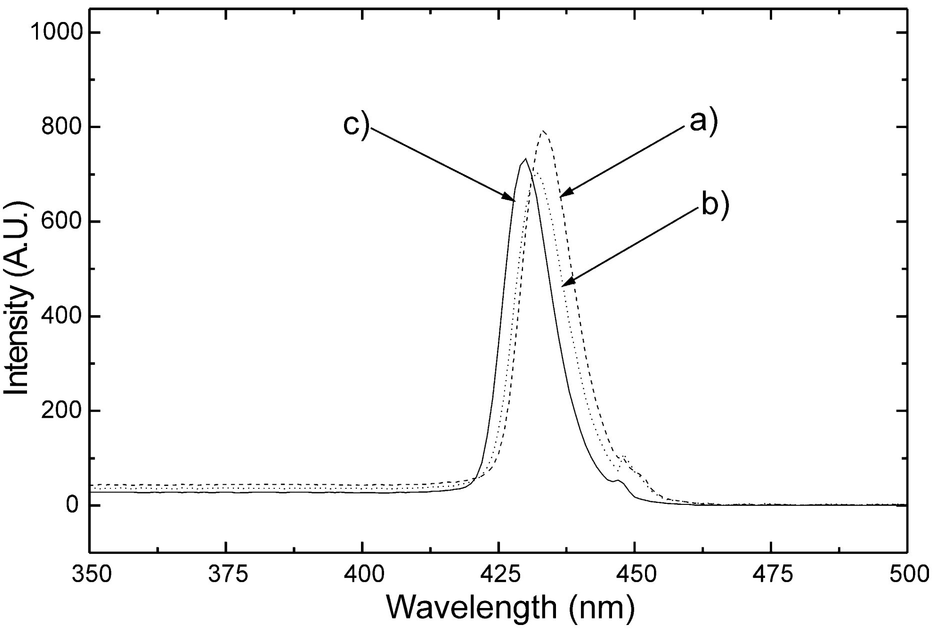


Fig. 2. Photoluminescent spectra of (a) model fluorophore **1**, (b) **3** and (c) **4**.

compound **1** and polymers **3** and **4** are presented in the Fig. 2. The polymers displayed blue photoluminescence in solution with maxima around 430 nm.

3.3. Chemiluminescence

Typical chemiluminescent studies were performed by mixing a solution of fluorophore and CPPO, and a solution of the catalyst and hydrogen peroxide at 25 °C. Chemiluminescence occurs, when the tube is bent. After the glass capillary tube is broken and the mixture is shaken for 2 min, the fluorophore solution is activated instantly by the catalyst solution. The emission spectrum were scanned at 2 min after the two components were mixed. The results of chemiluminescent spectra obtained were longer than normal photoluminescence spectrum excited at 366 nm of ultraviolet light. Chemiluminescent emissions spectra of **1**, **3** and **4** appeared around 440 nm as shown in Fig. 3. Typical blue light emissions have been observed from them. The wavelength of the emitted light is dependent on the substituent as an auxochromophore in the fluorophore [12]. In the previous paper, polyether isolated with alkyl spacer and distyrylarylene showed blue emission (λ_{max} = 470–495 nm) [4,6]. In this experiment, polymers 3 and 4 having anthracene moiety were moderate blue light-emitting fluorophores. Table 3 shows a chemiluminescent emission light of fluorophore **1**, **3** and **4** in the CIE chromaticity diagram.

When the polymer sample was compared with model compound **1**, similar results were observed. But the polyester emits blue light having broad wavelength range.

With regard to the practical usage of the blue anthracene dyes **3** and **4**, it is worth studying their peroxide degradation. It is required that the fluorescent dye should be stable in the presence of hydrogen peroxide. The 9,10-diphenylanthracene units have been known to be resistant to peroxide oxidation, but the fluorophores emitted a light with small change of CIE chromaticity value during chemiluminescent reaction. In the cases of model fluorophores **1** and **3**, CIE chromaticity value from $x = 0.1438$, $y = 0.0752$ and $x = 0.1593$, $y = 1.1512$ to $x = 0.1651$, $y = 0.1563$ and $x = 0.2092$, $y = 0.1959$, respectively.

A typical chemiluminescent decay curve for all the polymeric fluorophores in DBP shows a rapid decay during the first 25 min followed by a much

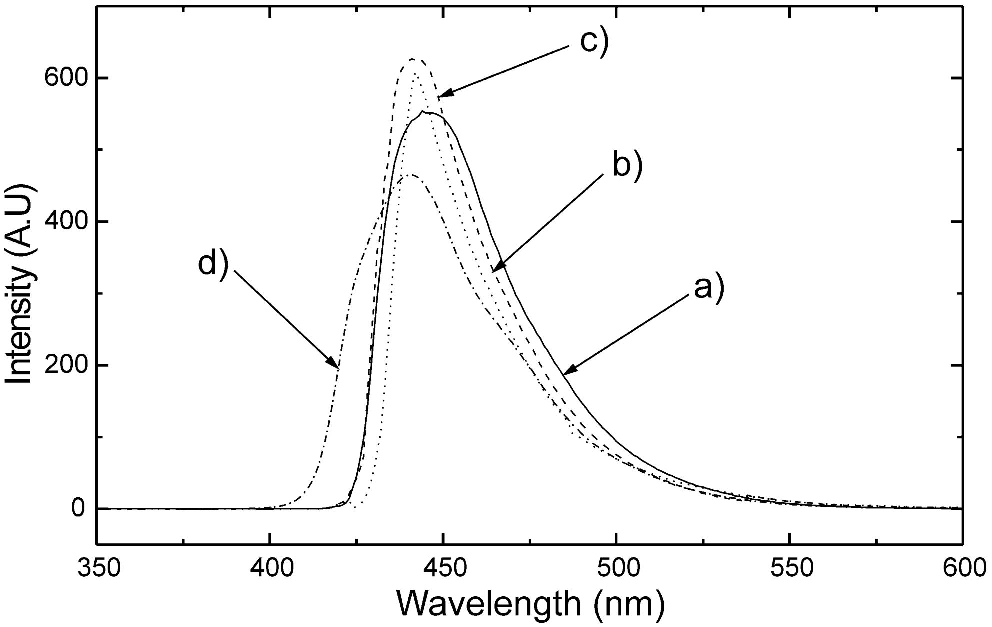


Fig. 3. Chemiluminescent spectra of (a) model fluorophore **1**, polymeric fluorophores (b) **3**, (c) **4** and (d) polymers obtained from 9,10-bis(p-hydroxyphenyl)-2-chloroanthracene and sebacoyl chloride.

slower decay lasting over 12 h. A similar, but much brighter chemiluminescent decay pattern was observed for model compound.

While the origin of the distinctive decay mode is well-defined at this time. It was known that the higher the initial emission intensity, the shorter is the life time. The very fast decay of the chemiluminescent intensity may be explained as due to the very fast reaction between CPPO and hydrogen peroxide, and the very high surface in the heterogeneous solvent system. We speculate that the initial burst is controlled by the component of solvents, therefore we used dimethylphthalate/*t*-butanol (v/v, 5/1) as a catalyst solvent [13–16]. These decay profiles can be fitted to exponential rate curve and accord with the intermediate model as shown in Table 4.

The decay intensities of the chemiluminescence for the polymeric fluorophores are showed in Fig. 4. Chemiluminescent emission was maintained for more than 12 h and was visible with naked eye. The maximum brightness of CL is ca.16–19 cd/cm^2 and 2–3 cd/cm^2 after 2 min and after 1 h, respectively. The other polymeric fluorophores with different alkyl structure were now in progress.

Table 4
The results of the chemiluminescent light decay characteristics of the model and polymeric fluorophores

Fluorophores	Decay equation	Light intensity (cd/cm^2) after min					
		0	2	30	60	100	150
1	$26.3995e^{-0.4673t}+5.0017e^{-0.0266t}$	31.5	16.8	3.53	2.53	2.01	1.51
3	$26.6214e^{-0.3085t}+2.4536e^{-0.0107t}$	29.0	17.1	3.34	2.24	1.88	1.36
4	$23.5416e^{-0.3762t}+4.8633e^{-0.0255t}$	28.3	18.5	2.74	2.40	2.14	1.61

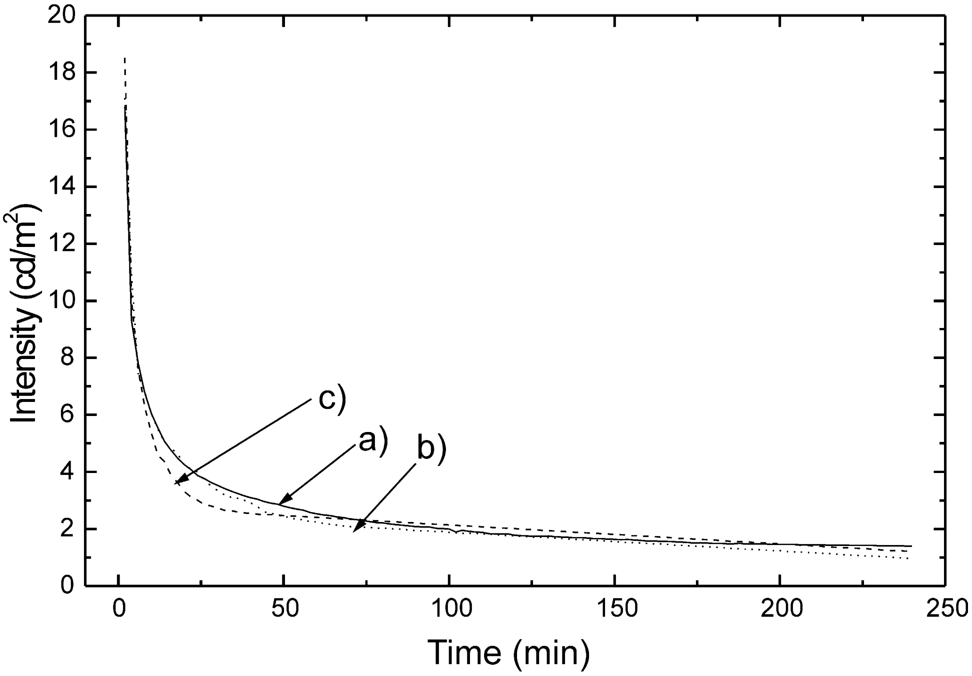


Fig. 4. Decay of the chemiluminescent light intensity of (a) model fluorophore **1**, (b) **3** and (c) **4**.

4. Conclusion

9,10-Diphenyl-2-chloroanthracene-containing polyether fluorophores with alkoxy spacer showed a good solubility in common organic solvents and were moderately stable under peroxide oxidative condition whereas it showed a little short decay time of which profiles fitted to exponential rate curve. They were applicable to the commercial blue fluorophore for the chemiluminescence. The color of fluorophores can be maintained from blue to sky blue through the chemiluminescent reaction.

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